

Objections to the Hotspot Model for the unidentified infrared emission bands of the interstellar medium

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ABSTRACT

We contest the ability of the interstellar dust Hotspot Model to explain the observed IR emission at short wavelengths of the ISM (interstellar medium). We show that both the theoretical and experimental bases of the model are not firm, and we perform a molecular dynamics calculation of the time needed for the energy of an absorbed photon to spread out in weakly bound HAC (hydrogenated amorphous carbon) solids that contradicts the prediction of the Hotspot Model.

Key words: line: formation – radiation mechanisms: thermal – dust, extinction – infrared: ISM: continuum – infrared: ISM: lines and bands.

1 INTRODUCTION

The so-called unidentified infrared bands (UIBs) are ubiquitous in our Galaxy and other external galaxies. They are always observed in emission, and the main features appear at 3.3, 6.2, 7.7, 8.6 and 11.3 μm . They are thought to come from a component of the ISM. After the strong suggestion by Duley & Williams (1981) that the 3.3- μm feature is likely to come from an aromatic CH stretch mode, Léger & Puget (1984) proposed that the *whole set of bands* could be produced by temperature fluctuations of free-flying large polycyclic aromatic hydrocarbon molecules (PAHs).

Many papers have since been devoted to the study of the consequences of this hypothesis (e.g. Allamandola & Tielens 1989). However, some confusion has arisen in other papers dealing with laboratory experiments on dust analogues and attempts to match the UIB pattern with measurements of absorption spectra. We believe that the identification of the interstellar component that produces the UIB cannot be completed from laboratory absorption spectra alone, unless the *emission mechanism* is explicitly proposed. For example, the 3.3- μm feature requires emitters at a colour temperature of 300 to 1000 K (Sellgren, Werner & Dinerstein 1983) far from the illuminating sources of radiation, where equilibrium temperatures of normal grains are much below that value.

Three emission mechanisms following the absorption of a photon have so far been discussed in the literature: (1) temperature fluctuations in isolated very small grains or large molecules (Andriessse 1978; Sellgren 1984; Léger & Puget 1984); (2) the Hotspot Model (Duley & Williams 1988)

where weakly linked islands in a grain have large temperature excursions; and (3) anomalous emissivity properties (coal model: Papoular et al. 1993; iron grains: Chlewicki & Laureijs 1988). We have addressed the third mechanism in a recent paper (Puget et al. 1995) and want to discuss the second one here. We want to show that, whereas the first emission model has been recently confirmed by laboratory experiments (Cherchneff & Barker 1989; Shan, Suto & Lee 1991; Brenner & Barker 1992), the second has neither a firm theoretical nor an experimental basis.

2 OBJECTIONS TO THE THEORETICAL BASIS OF THE HOTSPOT MODEL

The basis of the model has been given in a paper by Duley & Williams (1988). The authors consider an HAC grain made of numerous N -atom graphitic islands connected to one another by few chemical bonds (C atoms in sp^3 configuration). When a photon is absorbed in one of the islands (I_1), it excites an electronic transition and, shortly after, the energy is transferred to the vibrational modes, except for some possible visible fluorescence. Then, Duley & Williams estimate the time for half of the energy to migrate to another island (I_2) and compare it with the IR cooling time (~ 1 s). If the former is longer than the latter, the island radiates as a hotspot, and this model could explain the observed high colour temperature of the emission from the interstellar medium.

We now arrive at the crucial hypothesis of the model. To calculate the migration time, they *assume* that energy

migrates from island I_1 to island I_2 by excitation of the mode ν_0 of the bond between the islands (Fig. 1) and the transfer of energy quanta $h\nu_0$. In a simple scheme, one has $\nu_0 = (2\pi)^{-1}(k/M)^{1/2}$, where M is the reduced mass of a C-C oscillator and k is its bond stiffness. They estimate the rate at which such an excitation can occur and deduce the energy flow. When an energy E is distributed between the N atoms of an island, an associated temperature T can be derived (canonical or thermal approximation; see for instance Léger et al. 1989a). In the limit when this temperature is much larger than the Debye temperature of the system, it has the simple expression $kT \approx E/(3N-6) = \varepsilon$. The probability for mode ν_0 to be excited is given, in the thermal approximation, by the Boltzmann factor. The rate of vibrational energy exchange between modes is of the order of 10^{12} s^{-1} , so the energy $\Delta = h\nu_0$ is transferred from island I_1 to island I_2 at rate $R \sim 10^{12} \exp(-\Delta/\varepsilon) \text{ s}^{-1}$. The transfer from I_1 to I_2 of half the initial energy is then achieved after

$$\tau \sim 10^{-12} E(2\Delta)^{-1} \exp(\Delta/\varepsilon) \text{ s}. \quad (1)$$

To obtain times of the order or longer than the IR radiation cooling time ($\sim 1 \text{ s}$), they consider a frequency ν_0 and a number of atoms N such that the exponential term overcompensates the 10^{-12} pre-factor. This is the case, for instance, for $E = 10 \text{ eV}$, $\Delta = h\nu_0 = 0.4 \text{ eV}$ and $N = 300$ atoms, which lead to $\tau = 4 \times 10^4 \text{ s}$.

At first sight, this model seems simple but plausible. A more careful study of the assumptions, however, has led us to the conclusion that the model is incorrect, as explained hereafter. We think that to assume that the bond A-B between the two islands (Fig. 1) must be excited for the energy to flow from one to the other is *not correct*. When island I_1 is vibrationally excited, to transfer energy to island I_2 the atom A has to communicate motion to atom B, but this does *not* require a *relative* motion between A and B and therefore an excitation of the mode ν_0 .

This point is clearly demonstrated in the limit of a rigid rod A-B ($\nu_0 \rightarrow \infty$). Such a rod can transmit efficiently the motion of A to B and transfer energy from I_1 to I_2 , whereas the Hotspot Model predicts no energy transfer because the mode $h\nu_0$ cannot be excited (the Boltzmann factor vanishes in the limit $h\nu_0 \rightarrow \infty$). *The result of this model is paradoxical indeed, as the stiffer the bond, the less efficient is the coupling between the two assemblies of oscillators!*

We therefore conclude that the theoretical basis of the Hotspot Model is incorrect.

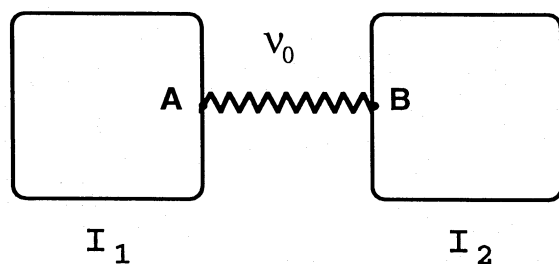


Figure 1. Two islands, each containing N atoms of mass M , are connected by a bond with stiffness k and frequency $\nu_0 = (2\pi)^{-1}(k/M)^{1/2}$. Energy is initially localized in island I_1 , and the problem is to estimate the time τ for energy to be statistically distributed between the two islands.

3 NUMERICAL SIMULATION OF THE ENERGY REDISTRIBUTION BETWEEN TWO ISLANDS OF A GRAPHITIC GRAIN

To estimate the actual time for energy diffusion, we have made a molecular dynamics calculation of the energy redistribution between two islands connected by a bond with stiffness k , after one island has absorbed a 10-eV photon.

The system considered is planar and made of two 240-atom islands (see Fig. 2). A hexagonal geometry is chosen with the atom-atom equilibrium bond distance $r_0 = 1.40 \text{ \AA}$ to represent an aromatic structure. The same value of r_0 is chosen for the bond connecting the islands (this distance is made longer in Fig. 2 for clarity). A single stretching potential between adjacent atoms (i.e. centres of forces) is used:

$$U(r_{C-C}) = (1/2)k(r_{C-C} - r_0)^2. \quad (2)$$

The stiffness k_0 of the bonds within the islands is representative of aromatics: $5.435 \text{ mdyn \AA}^{-1}$ (Cyvin, Brunvoll & Cyvin 1984). The corresponding vibrational energy quantum is $h\nu_0 = \Delta = 0.08 \text{ eV}$. Different values for the stiffness of the

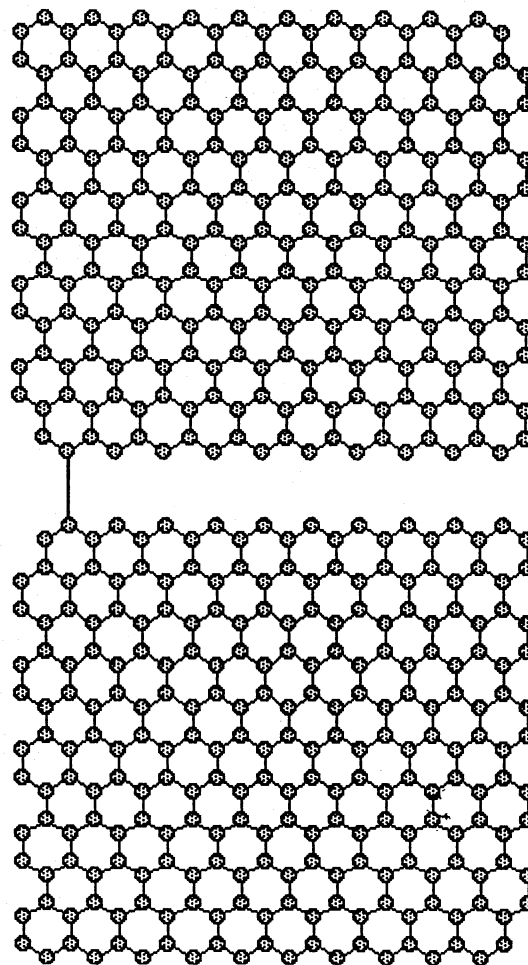


Figure 2. Schematic view of the planar model of two aromatic islands of 240 carbon atoms each, connected by a single bond. In this drawing the connecting bond length is made longer for clarity, but, in the simulation, a single equilibrium bond length was used whatever the neighbour atoms.

bond connecting the islands are considered in order to simulate covalent and weaker bonding (e.g. van der Waals bondings):

$$k_1 = k_0, \quad \Delta = 8 \times 10^{-2} \text{ eV}$$

$$k_2 = 10^{-1} k_0, \quad \Delta = 2.5 \times 10^{-2} \text{ eV}$$

$$k_3 = 10^{-2} k_0, \quad \Delta = 8 \times 10^{-3} \text{ eV}$$

$$k_4 = 10^{-3} k_0, \quad \Delta = 2.5 \times 10^{-3} \text{ eV}$$

$$k_5 = 10^{-4} k_0, \quad \Delta = 8 \times 10^{-4} \text{ eV}$$

The microcanonical classical equations of motions are integrated using the Verlet algorithm. A time step of 10^{-16} s is used (similar results were obtained with 10^{-17} s). For each run corresponding to a particular stiffness value of the connecting bond k_n ($n = 1$ to 5), 10 eV of energy is initially distributed among the atoms of one of the islands [i.e. each atom has an initial velocity corresponding to a kinetic energy of (10/240) eV, in addition to its zero-point energy]. For the sake of simplicity, the initial kinetic energy of the other island is fixed to be zero.

The resulting total energies (kinetic + potential) of both islands as a function of time are shown in Fig. 3 for the runs using k_1 , k_3 and k_5 values. Whatever the stiffness of the connecting bond, the time needed for a complete redistribution of the energy (60–4000 ps) is *much shorter* than that estimated by Duley & Williams (1988) and *does not allow significant IR emission from the hot island*.

The redistribution time τ is plotted as a function of the connecting vibrational quantum Δ in Fig. 4. We find a Δ^{-1} dependence. *In contrast to Duley & Williams' result, we find that a stiffer bond makes the coupling between islands more efficient*. The limit of an extremely weak bond corresponds to an isolated island, i.e. a free-flying molecule. To obtain the required time, $\tau = 1$ s, however, the bond has to be unrealistically weak, i.e. $\Delta = h\nu_0 = 5 \times 10^{-12}$ eV or $\nu_0 = 1.2 \times 10^3$ Hz, corresponding to a binding energy of less than 10^{-18} eV, far weaker than any van der Waals bond.

The preceding calculation is classical in nature although expressed as a function of the quantum vibrational energy of the bond: $\Delta = h(2\pi)^{-1}(k/M)^{1/2}$. This could be considered as a limitation. A quantum calculation of the time evolution of vibrational energy in a crystal of a PAH (naphthalene) by Dlott (1989), however, leads to a similar result: the energy initially localized in a molecular skeleton mode 1627 cm^{-1} is completely spread into low-energy phonons that imply motion of the whole crystal, in less than 10^{-9} s (see also Tielens 1993). A similar result has been obtained by Boissel et al. (1987) for the duration of the localization of vibrational energy in an SF_6 molecule in rare gas matrices, a case of a molecule weakly bound to its surroundings.

The result of this molecular dynamics simulation confirms the conclusion of Section 2.

4 ON THE EXPERIMENTAL BASIS OF THE HOTSPOT MODEL

It is our opinion that experiments do not support the Hotspot Model either. There is *a considerable gap* between the times during which energy is measured to be localized in hotspots in the laboratory and those that would be required to support the model. As an example, the work of Malinovsky

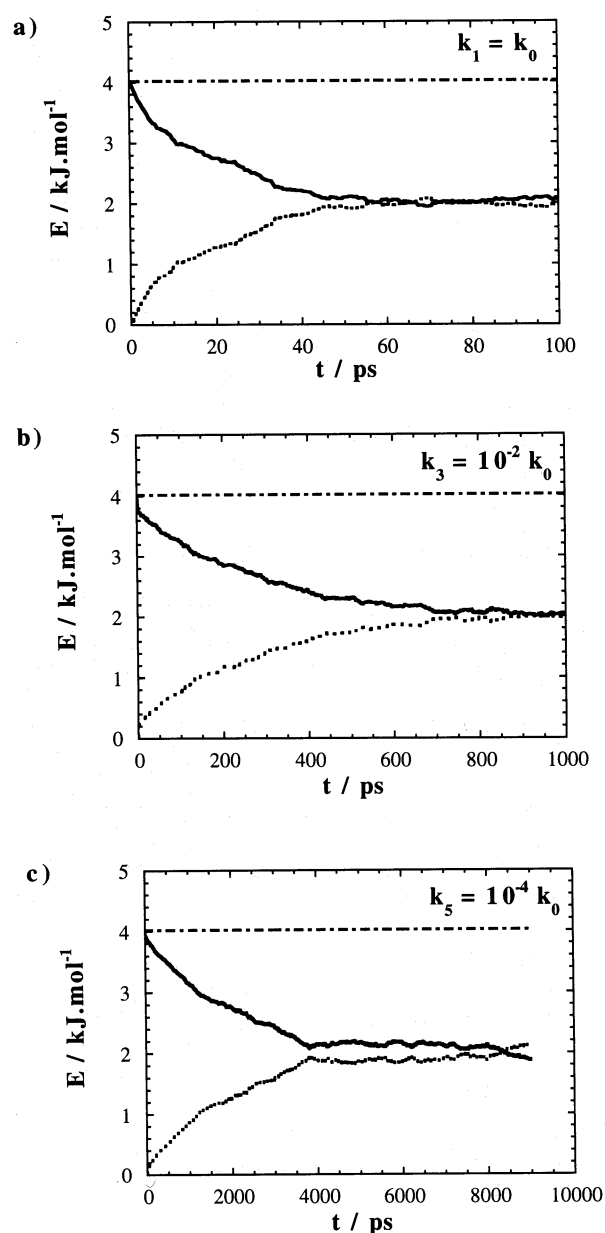


Figure 3. Total energy (kinetic + potential), per carbon atom, of each of the islands as a function of simulation time, using stiffness values of the connecting bond $k_1 = k_0$ (a), $k_3 = 10^{-2} k_0$ (b) and $k_5 = 10^{-4} k_0$ (c), where k_0 is the aromatic stretch C–C stiffness, $k_0 = 5.45 \text{ mdyn } \text{Å}^{-1}$. Initial energy is 10 eV (961 kJ mol^{-1}) in one island ($4.17 \times 10^{-2} \text{ eV} = 4 \text{ kJ mol}^{-1}$ per atom) and 0 in the second. In each plot the full line corresponds to the initially hot island and the dotted line to the cold one. The horizontal dash-dotted line corresponds to the sum of the energies of the two islands. From these plots we estimate the redistribution times as 6×10^{-11} s for k_1 , 9×10^{-10} s for k_3 and 8.5×10^{-9} s for k_5 . Note the statistical fluctuations of energies in addition to the mean tendency to equipartition.

(1987) is quoted by Duley & Williams (1988). The former author describes a local heating of subunits in amorphous materials with sizes of the order of 10 Å . He interprets the laboratory data with a model where phonons can be localized in small regions and diffuse ‘slowly’ at the expense of phonon–phonon interaction. Malinovsky states that the time

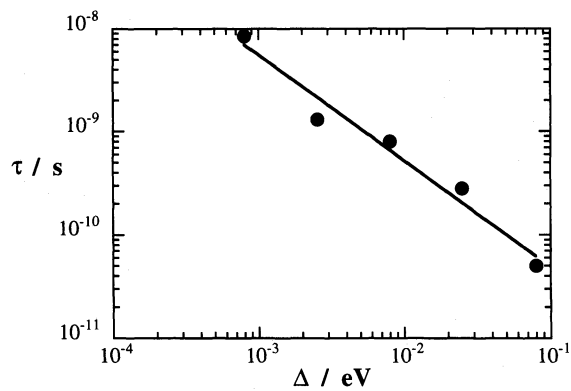


Figure 4. Redistribution times of the 10-eV energy as a function of the bond vibration energy quantum Δ , in a log-log plot. The solid line is the result of a least-squares fit; its slope is equal to -1.03 with a regression coefficient of 0.98.

of localization can exceed a characteristic phonon period (3×10^{-14} s) by 2–3 orders of magnitude and that ‘a great part of energy [...] will belong to localized vibrations and stay in the micro region for a time greater than 10^{-11} s’. This time is longer than 10^{-11} s by a factor of a few units but not by *11 orders of magnitude* as would be required by the Hotspot Model. The time is sufficient to produce (fast) structural changes that can modify the semiconductor optical properties, as observed in As_2S_3 glasses (Malinovsky 1987), but not to emit IR photons, which requires times of the order of 1 s (Duley & Williams 1988; Léger, d’Hendecourt & Défourneau 1989b). Therefore, such work *cannot be considered as providing experimental support* for the Hotspot Model for IR emission.

All the failed attempts made in physical chemistry to localize energy in molecules for times longer than 10^{-11} s (e.g. Hutchinson et al. 1983) also point in the same direction.

5 CONCLUSION

We argue that the Hotspot Model for IR emission has neither valid theoretical basis nor experimental support, that it can-

not be invoked to explain the high colour temperature IR emission from the ISM (Sellgren et al. 1983) and that it is not a plausible alternative to the Temperature Fluctuation Model of ‘free-flying’, very small grains or large molecules (Andriessse 1978; Sellgren 1984; Léger & Puget 1984).

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